

Study of the second harmonic emission of glycine-sodium nitrate crystals at different pH

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Abstract

This work shows an optical and structural study of glycine sodium nitrate crystals. This study was supported with the respective X ray diffraction and Second-Harmonic Generation signal detection by using a little variant to the Kurtz- Perry method. The goal of this work is to obtain the right pH that modifies the charge of glycine sodium nitrate system in order to obtain the best second harmonic emission. Furthermore, with the change on the charge on the aminoacid, it is observed how it modifies the optical properties in the glycine sodium nitrate complex.

Keywords: RAMAN, GSN, NLO, SHG, pKa

Introduction

Nonlinear optical (NLO) materials have wide applications in the area of laser technology, optical communication and electro optics application. The nonlinear optical effect is the interaction of an electromagnetic field of high intensity laser light with a material [1-3]. The development of photonic and optoelectronic technologies rely heavily on growth of NLO materials with the high light no linear responses. A NLO material need to have a large NLO coefficient, large birefringence, wide transparency range, high damage threshold, broad spectral and temperature bandwidth, good chemical and mechanical stability, ease of growth and low cost [4-6]. One of the advantages in

working with organic materials is that they allow one to fine-tune the chemical structures and properties for the desired nonlinear optical properties. Additionally, they have large structural diversity. The properties of organic compounds can be refined using molecular engineering and chemical synthesis [6]. The second harmonic generation SHG is a phenomenon produced by the second order nonlinearities in a material when it is exposed to high intensity and monochromatic light source. Given glycine amino acids as an amphoteric, it can be assumed as cationic, anionic and zwitterionic configurations, *i.e.* the charge distribution is determined by the pH and the pKa of the carboxylic group (pKa = 2.34) and the amino group (pKa = 9.6). Thus, in the pH range between 2.34 and 9.6, most of molecules are zwitterionic with both ends charged NH_3^+ and COO^- [1,7,8]. Additionally the study of the effect on the pH on the complex GSN can provide the correct way to rowth crystals based on aminoacids with a good morphological quality and excellent optical properties.

Experimental

Crystal Growth

The GSN crystals were obtained by using 99.9% purity Sigma Aldrich glycine ($\text{NH}_2\text{-CH}_2\text{-COOH}$) with FW = 75.57 g/mol, and Sigma Aldrich sodium nitrate (NaNO_3) (99.9%) with FW = 4.99 g/mol. A stoichoimetric mixture of glycine and sodium nitrate in equimolar ratio was dissolved in 100ml of water distillated with stirrer magnetic in a thermoplate. In order to modify the charge of GSN molecule, seven samples with different pH (1,3,4,7,9, 10,11) were prepared [10]. In this sense we have obtained three electric glycine configurations (Zwitterionic, Cationic, and Anionic). The pH was adjusted with nitric acid concentrate HNO_3 and ammonium hydroxide NH_4OH . As follow step the

crystals were retired of the solution are washed with distilled water and immediately drying to prevent clusters formation, crystalline inclusions and eliminate impurities on surfaces. Hence, the size and quality of crystals dependent on the molar ratio in the reagents compared with the solvent, *i.e.* for low concentrations, crystals are big and for high concentrations, crystals are small.

Characterization

Crystal Growth

GSN crystals were obtained by a slow evaporation technique for aqueous solutions. The crystals were prepared with distilled water containing glycine, Sodium Nitrate [NaNO₃] in molar ratio 1:1 with a starting pH of 6.4, and then changing the pH of the solution at 1,3,4,7,9,10,11.

Transparent crystals of different size and shapes were obtained in about two to three weeks at room temperature. The size of the crystals was found to be depending on the amount of material available in the solution which in turn is decided by the solubility of the material in solvent. The shapes were found to be determined by the pH of the solution. Figure 1 displays the micrographs of crystals grown at different pH.

RAMAN Spectroscopy

The RAMAN spectroscopy is a powerful technique used for the analysis of organic compounds which is useful for any state of matter and especially in biological samples. Other advantage of RAMAN spectroscopy is the use of visible radiation, this allows narrow down the warming effects in the sample[11]. The RAMAN spectra can be identified as roto-vibrational spectra, because the lines of RAMAN frequency correspond to the distance between energy levels. Hence, the main transitions are due

to the normal vibrational modes and determinate the modes that change the polarization in the molecule, this characteristic is the main reason why RAMAN is useful in the analysis of GSN [12]. In the present work the RAMAN spectra was carried out at room temperature in frequency range $400 - 4000 \text{ cm}^{-1}$ with Xplora RAMAN microscope HORIBA system.

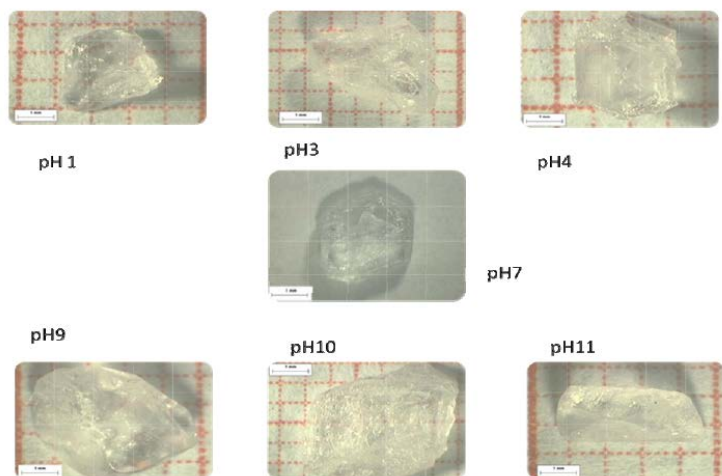


Figure 1. Single crystals of GSN recrystallized at different pH.

The Figure 2 shows the symmetric and asymmetric of the functional group NH_3^+ and the stretching vibrations found in 3244 y 2884 cm^{-1} frequency. Furthermore, the position and broadness of this mode, 3 NH_3^+ asymmetric stretching frequency, indicate the formation of both, intra and intermolecular strong N-H—O hydrogen bonding of the NH_3^+ group, with the oxygen of both, the carbonyl group and inorganic nitrates. Hence, the presence of this bonds make what are found lowering frequencies 2884 cm^{-1} [4,13]. The crystal structure of GSN show that the organic molecular units are located between layers of NaNO chains and linked to sodium nitrate by strong intramolecular hydrogen bonds of N-H—O type. This structural organization of infinite chains of highly polarity entities connected in a head to tail arrangement in GSN is behalf in contribution to the

NLO properties of the crystal. The study of symmetry and stretching vibration of CH₂ group is observed around 3023 and 2969 cm⁻¹. The CH and NH bending observed in 1616 and 1510 cm⁻¹ frequency. The absorption peaks at 2009 and 1615 cm⁻¹ confirmed the presence of 3 NH₃⁺ bending. The peak at 1408, 586 and 509 cm⁻¹ is assigned to the symmetric stretching C-COO carboxyl group. The band around 1118 cm⁻¹ is also indicative of the NH₃ rocking modes. The band around 178 cm⁻¹ it is indicative of torsion of Na. The wavelength was observed and the proposed allocation of spectrum is shown in the following Table 1.

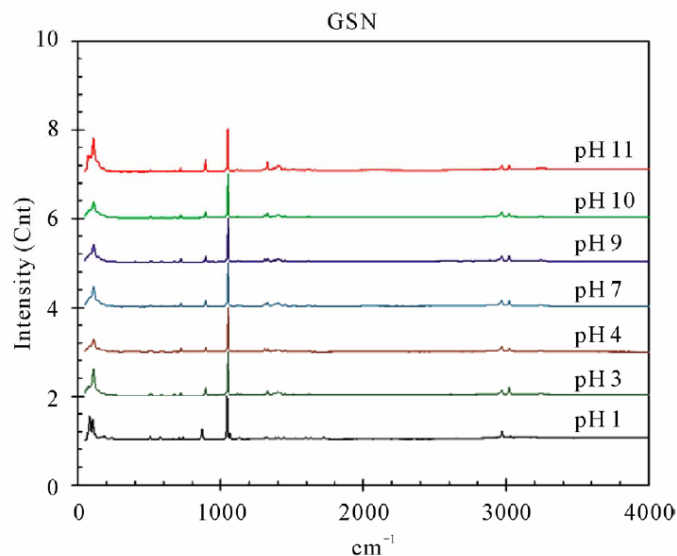


Figure 2. The RAMAN spectra of GSN at different pH.

X-Ray diffraction

In order to obtain the structural parameters of the crystal under study, we also achieve a powder X ray diffraction to confirm the phase. The analysis of the observed spectra was performed using X'Pert data collector, powder diffraction data interpretation and indexing software program X'Pert Highscore Plus. Version 2.2a. The XRD peaks were indexed and the unit cell was found to have monoclinic symmetry with cell

parameters $a = 14.326 \text{ \AA}$, $b = 5.261 \text{ \AA}$, $c = 9.115 \text{ \AA}$, $\beta = 119.070$ and unit cell volume of 600.45 \AA^3 . The Figure 3 showed that basic pH obtained the major phase of GSN compared with acid pH. This is because, as the pH becomes more acid, the diffraction patterns show that it reduces the phase of GSN and other compounds are generated.

Similar information has been reported for the authors elsewhere [14] in the L-alanine sodium nitrate. Also a slow overtone signal in the NH_3 group is characteristic of the nonlinear emission.

Table 1. Raman assignment.

Frequency RAMAN/ cm^{-1}	Assignment
3243	NH_3^+ Asym Strech
3024	CH_2 Asym Strech
3000	?-Glycline
2976	CH_2 Sym Strech
2884	N-H...O Sym Strech
2725	overtones
2616	overtones
1659	Overtones
1614	NH_3^+ Asym Bend
1508	NH_3^+ Sym Bend
1448	CH_2 Scissoring
1397	NO_2^- Asym Strech
1329	CH_2 Wagging
1309	CH_2 Wagging
1143	CH_2 Twisting
1114	NH_3^+ Rocking
1052	NO_2^- Sym Strech
939	CH_2 Rocking
895	C-C Strech
723	COO^- Deform
677	NO_2^- inplane Deform
588	COO^- Deform
508	COO^- Rocking
398	NH_3^+ Torsión
330	CCN Bending
178	Na^+ Translation
138	COO^- Torsion
109	N...O Vibrations

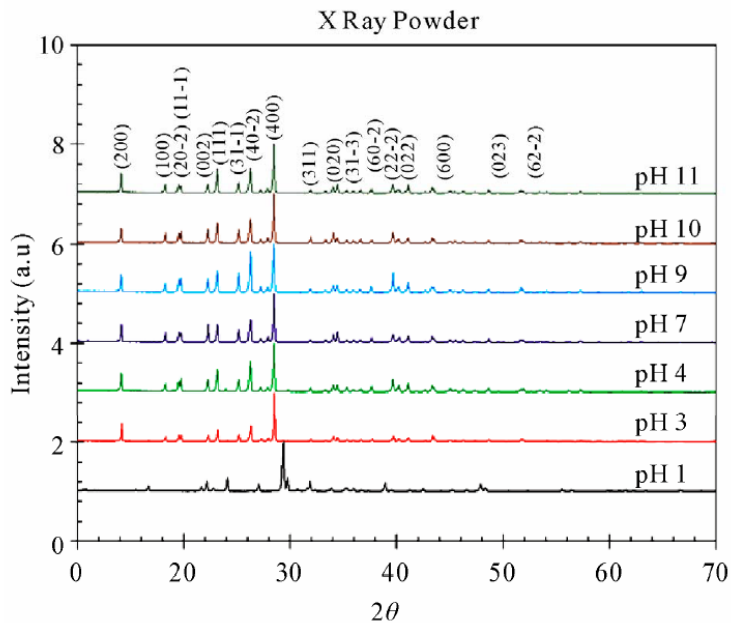


Figure 3. The X-ray pattern for GSN at different pH.

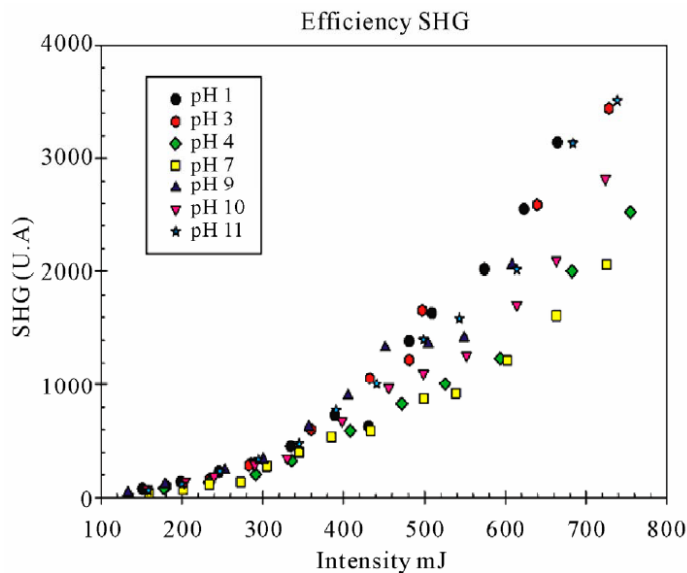


Figure 4. The SHG signal of GSN at different pH.

Second-Harmonic Generation

Second-harmonic generation (SHG), or frequency doubling, can be defined as the conversion of a specific wavelength of light into half its original λ_1 $1/2 \lambda_1$, or with

respect to frequency ω , ω_1 $2\omega_1$. A typical setup for power SHG measurements is made for modified Kurtz- Perry method. Also, a low energy laser, pulsed or continuous, is needed. [2,14,15] Usually Nd-YAG laser (1064 nm output) is used and the sample is a polycrystalline powder. With normal size of 70 μm each crystal, is shown the SHG measurements with respect to different pH of GSN from 1 to 11. Figure 4 shows the efficiency of GSN samples at different pH.

The SHG efficiencies are pH 3 this due is closer to $\text{pK}_a = 2.3$ of glycine and the dipole moment is majorly due to the change of charge of the molecule, however the change in the dipole moment of the molecule above of $\text{pK}_a = 9.7$ also shows a good efficiency, it is given that the sample with more acid pH showed that contains γ -glycine and the more basic pH showed that contains GSN phase in more concentration.

The transparent glycine sodium nitrate crystals (GSN crystals) were successfully obtained using slow evaporation technique at room temperature and we characterized them by various techniques. The presence of fundamentals groups was verified by a RAMAN microscope. The GSN structure was characterized using XRD powder, the X-ray pattern showed that the samples of GSN to basic pH contained the GNS phase and the more acid pH is observed that is obtained GSN on minor concentration but too obtain subproducts like γ -glycine which increase the efficiency of SHG.

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